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<b>(21) International Application Number:</b> PCT/GB97/03404 <b>(22) International Filing Date:</b> 10 December 1997 (10.12.97)  <b>(30) Priority Data:</b> 08/770,753      19 December 1996 (19.12.96)      US  <b>(71) Applicant:</b> THE GENERAL ELECTRIC COMPANY, PLC [GB/GB]; 1 Stanhope Gate, London, W1A 1EH (GB).  <b>(72) Inventor:</b> ZHU, Linfang; 338 Meadow Green Drive, Naperville, IL 60565 (US).  <b>(74) Agent:</b> MCGOWAN, Nigel, George; GEC Patent Dept., Waterhouse Lane, Chelmsford, Essex CM1 2QX (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> A JET INK COMPOSITION  <b>(57) Abstract</b> <p>Disclosed is a jet ink composition suitable for printing marks on metal, glass, plastics, rubber, or paper comprising an ink carrier, a fluorescent colorant, a cellulosic binder resin, and a tetraalkyl ammonium or phosphonium salt. The jet printed marks do not blush, bleed, or fade, as a result of exposure to steam, or hot and cold water. Also disclosed is an improved process of jet printing on substrates comprising printing with the disclosed jet ink composition.</p>		

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## A JET INK COMPOSITION

The present invention generally relates to ink jet printing fluorescent ink compositions, and particularly to ink jet printing fluorescent ink compositions whose marks resist blushing, bleeding, or fading as a result of exposure to water.

Ink jet printing is a well-known technique by which printing is accomplished without contact between the printing device and the substrate on which the printed characters are deposited. Briefly described, ink jet printing involves the technique of projecting a stream of ink droplets to a surface and controlling the direction of the stream electronically so that the droplets are caused to form the desired printed image on that surface. This technique of noncontact printing is particularly well suited for application of characters onto irregularly shaped surfaces, including, for example, the bottom of glass, metal, or plastic containers, used for holding cosmetic, pharmaceutical, liquor, and health care products.

Reviews of various aspects of ink jet printing can be found in these publications: Kuhn et al., *Scientific American*, April, 1979, 162-178; and Keeling, *Phys. Technol.*, 12(5), 196-303 (1981). Various ink jet apparatuses are described in the following U.S. Patents: 3,060,429, 3,298,030, 3,373,437, 3,416,153, and 3,673,601.

In general, an ink jet ink composition must meet certain rigid requirements to be useful in ink jet printing operations. These relate to viscosity, resistivity, solubility, compatibility of components and wettability of the substrate. Further, the ink must be

quick-drying, smear resistant, and be capable of passing  
5 through the ink jet nozzle without clogging, and permit  
rapid cleanup of the machine components with minimum  
effort.

The marking of articles such as bank checks,  
envelopes, certificates, and the like, as well as food  
10 containers such as metal, plastic or glass containers  
with identification marks for later identification and/or  
sorting is well known. Several methods have been  
proposed for producing such security or identification  
marks. For example, infrared readable bar codes have  
15 been proposed. See, e.g., Japanese Patent Application  
Kokai No. 58-45999 and U.S. Patent 5,366,252.

The methods based on infrared readable materials  
have the disadvantage that the infrared absorbing bar  
codes are to some extent visible to the unaided eye and  
20 need to be physically concealed. The concealment of the  
bar code results in covering up of a portion of the  
article, thereby adversely affecting the aesthetics of  
the article.

Fluorescent materials have been considered for  
25 marking purposes. It is known that fluorescence is the  
property of a material to emit radiation as the result of  
exposure to radiation from some other source. The  
emitted radiation persists only as long as the exposure  
is subjected to radiation. The fluorescent radiation  
30 generally has a wavelength longer than that of the  
absorbed radiation.

There has been significant developmental activity in  
the area of fluorescent jet inks for producing security  
marks on envelopes and documents. For instance,  
35 U.S. Patent 5,093,147 discloses a method for providing  
intelligible marks that are virtually invisible to the  
unaided eye on the surface of an article. The method  
employs a jet ink containing an organic laser dye that is

poorly absorptive in the visible range of about 400 to  
5 700 nm, is absorptive of radiation in the near infrared  
range of at least 750 nm, and fluoresces in response to  
radiation excitation in the infrared range at a  
wavelength longer than that of the exciting radiation.

U.S. Patent 4,736,425 discloses a method of marking  
10 fiduciary documents requiring authentication by the use  
of certain fluorescent chelates. The method comprises  
introducing only a part of the elements forming the  
chelate onto the document to be marked and subsequently  
contacting the document for authentication purpose with  
15 the missing part of the elements forming the chelate to  
effect the synthesis of the fluorescent chelate. The  
chelate thus formed is excited by ultraviolet radiation  
and the resulting fluorescence radiation is detected.

U.S. Patent 4,450,595 discloses a jet ink that can  
20 be used to mark documents such as bank checks for  
automatic identification. The ink contains certain  
phenoxazine derivative dyes that are visible to the  
unaided eye and fluoresce in the near infrared region  
(650 to 800 nm) upon activation using an activating light  
25 having a wavelength in the range of 550 to 700 nm. The  
ink that is visible to the unaided eye is unfortunately  
not suitable for many security mark applications.

Commonly owned and copending U.S. patent application  
Serial No. 08/661,180, filed June 10, 1996, discloses jet  
30 ink compositions suitable for marking on white or light  
colored substrates such as envelopes. The ink  
composition comprises a fluorescent colorant and an ink  
carrier. The colorant comprises a rare earth metal and a  
chelating agent. The mark produced by the ink  
35 composition is completely or substantially invisible to  
the unaided eye and is visible only when excited by  
ultraviolet light.

Metal containers such as, for example, empty

containers used to can foods or beverages such as coffee,  
5 beer, soup, and others are shipped to the fillers with  
identification marks placed thereon by the container  
manufacturer. At the fillers' premises, the containers  
are subjected to various treatments including autoclaving  
in presence of steam, and immersing the containers in  
10 water. The autoclaving is carried out at temperatures as  
high as 250°F for times up to 30 minutes. The immersion  
testing typically is carried out by immersing the  
containers in selected temperature waters ranging from  
ice water to boiling water for a period ranging from  
15 about 5 minutes to about 30 minutes. It has been a  
problem with some of the previously known fluorescent jet  
ink compositions that the marks tend to blush, bleed, or  
fade as a result of one or more of these treatments.  
When the mark becomes visible to the unaided eye, it is  
20 said to have blushed. When the mark becomes diffuse, it  
said to have bled. When the mark becomes unreadable or  
poorly readable due to reduced color intensity, it is  
said to have faded.

In the area of marking objects such as metals, the  
25 following publications are of interest. German Patent DE  
3529798 reportedly discloses a jet ink for placing on  
metals, plastics, paper, or glass identification marks  
that are invisible to the naked eye consisting of an  
alcohol solvent, a fluorescent substance that is soluble  
30 in a water/ethanol mixture, a water-soluble polyacrylate,  
and optionally a water-soluble cellulose ester and  
diethanolamine.

German Patent DE 4013456 reportedly discloses a jet  
ink containing an organic solvent, a fluorescent  
35 dyestuff, a polyamic acid or polyimide binder resin, and  
conductive salts. The ink is said to adhere well to  
glass, ceramic, and copper.

Commonly owned and copending U.S. patent application

Serial No. 08/686,191, filed July 26, 1996, discloses a  
5 jet ink composition suitable for producing blush  
resistant marks that are invisible to the unaided eye and  
are visible only when excited by an exciting radiation  
comprising a solvent, a fluorescent colorant, a binder  
resin, and a plasticizer having a vapor pressure of about  
10 15 mm Hg or less at 240 °C.

The foregoing indicates that there exists a need for  
a jet ink composition comprising a fluorescent colorant  
suitable for printing identification marks on metals,  
glass, ceramics, and plastics.

15 Thus, there exists a need for a jet ink composition  
suitable for printing on substrates, particularly metal  
containers, marks that resist blushing. There also  
exists a need for a jet ink composition suitable for  
printing on substrates, particularly metal containers,  
20 marks that resist bleeding. There also exists a need for  
a jet ink composition suitable for printing on  
substrates, particularly metal containers, marks that  
resist fading.

The present invention provides a jet ink  
25 composition comprising a fluorescent colorant suitable  
for printing identification marks on metals, glass,  
plastic, ceramics, or paper.

The jet ink composition of the present invention  
comprises an ink carrier, a fluorescent colorant, a  
30 cellulosic binder resin, and a tetraalkyl ammonium or  
phosphonium salt.

The marks printed using the inventive jet ink  
composition have at least one, and preferably more than  
one, advantage. These advantages are blush resistance,  
35 bleed resistance, and fade resistance.

The present invention further provides an improved  
process of jet printing on metal, glass, plastic, rubber,  
or paper substrates. The improvement comprises

projecting a stream of ink droplets of a jet ink  
5 composition to the surface of the substrates and  
controlling the direction of the stream electronically so  
that the droplets are caused to form the desired marks on  
the surface.

The present invention provides jet ink compositions  
10 suitable for printing marks that are invisible to the  
unaided eye and are visible only when excited by an  
exciting radiation.

The present invention further provides a jet ink  
composition suitable for producing blush resistant marks  
15 that are invisible to the unaided eye and are visible  
only when excited by an exciting radiation.

The present invention further provides a jet ink  
composition suitable for producing bleed resistant marks  
that are invisible to the unaided eye and are visible  
20 only when excited by an exciting radiation.

The present invention further provides a jet ink  
composition suitable for producing fade resistant marks  
that are invisible to the unaided eye and are visible  
only when excited by an exciting radiation.

25 In general, the jet ink composition of the present  
invention exhibit the following characteristics for use  
in ink jet printing systems: (1) a Brookfield viscosity  
of from about 1.6 to about 7.0 centipoises (cps) at 25  
°C; (2) an electrical resistivity of from about 20 to  
30 about 2000 ohm-cm; and (3) a sonic velocity of from about  
1100 to about 1700 meters/second.

A detailed discussion of the various components and  
a method of preparation of the inventive jet ink  
composition is set forth below.



FLUORESCENT COLORANTS

5 Any suitable fluorescent colorant that is substantially or completely invisible to the unaided eye can be used in the preparation of the inventive ink composition. The fluorescent colorant absorbs outside the visible range, and fluoresces at a wavelength longer  
10 than the absorption wavelength. Preferably, the fluorescent colorant absorbs in the wavelength region of from about 275 nm to about 400 nm and emits in the wavelength region of from about 420 nm to about 520 nm. A fluorescent colorant that emits a blue line is further  
15 preferred.

An example of a suitable fluorescent colorant is 2,2'-(2,5-thiophenediyl)-bis(5-tert-butylbenzoxazole), which is available as UVITEX OB from Ciba-Geigy Corp. in Hawthorne, New York. UVITEX OB is a yellow crystalline  
20 powder having a melting point of 197-203 °C. It has good lightfastness, excellent resistance to heat, and high chemical stability. UVITEX OB can be heated for 8 hours at 300 °C in a nitrogen atmosphere without decomposition. The colorant also can be heated for the same period at  
25 200°C in air without decomposition. UVITEX OB has an absorption maximum at 375 nm (extinction coefficient 1,200 at 1%, 1 cm) and a fluorescence maximum at 435 nm when measured in ethanol solution. The colorant produces a blue fluorescence. UVITEX OB is known to be useful as  
30 an optical brightener in plastics.

Examples of other optical brighteners can be found in Kirk-Othmer Encyclopedia of Chemical Technology, 4, "Fluorescent Brighteners", pp. 213-225 (1978), and include the stilbene derivatives such as 4,4'-  
35 bis(triazin-2-ylamino)stilbene-2,2'-disulfonic acid derivatives wherein the triazinyl groups are substituted with suitable substituents, including substituents such

as anilino, sulfanilic acid, metanilic acid, methylamino,  
5 N-methyl-N-hydroxyethylamino, bis(hydroxyethylamino),  
morpholino, diethylamino, and the like; mono(azol-2-  
yl)stilbenes such as 2-(stilben-4-yl)naphthotriazoles and  
2-(4-phenylstilben-4-yl)benzoxazoles; bis(azol-2-  
yl)stilbenes such as 4,4'-bis(triazol-2-yl)stilbene-2,2'-  
10 disulfonic acids; styryl derivatives of benzene and  
biphenyl such as 1,4-bis(styryl)benzenes and 4,4'  
bis(styryl)biphenyls; pyrazolines such as 1,3-diphenyl-2-  
pyrazolines; bis(benzazol-2-yl) derivatives having as  
phenyl ring substituents alkyl, COO-alkyl, and SO<sub>2</sub>-alkyl;  
15 bis(benzoxazol-2-yl) derivatives; bis(benzimidazol-2-yl)  
derivatives such as 2-(benzofuran-2-yl)benzimidazoles;  
coumarins such as 7-hydroxy and 7-(substituted  
amino)coumarins, 4-methyl-7-amino-coumarin derivatives,  
esculetin,  $\beta$ -methyllumbelliferone, 3-phenyl-7-(triazin-2-  
20 ylamino)coumarins, 3-phenyl-7-aminocoumarin, 3-phenyl-7-  
(azol-2-yl)coumarins, and 3,7-bis(azolyl)coumarins;  
carbostyrils, naphthalimides, alkoxynaphthalimides,  
derivatives of dibenzothiophene-5,5-dioxide, pyrene  
derivatives, and pyridotriazoles.

25 Coumarin type fluorescent colorants can be obtained  
commercially from BASF Corp. in Holland, Michigan. Thus,  
coumarin is sold as CALCOFLUOR WHITE LD or Fluorescent  
Brightener 130, which has an absorption maximum at 367.8  
nm and an emission maximum at 450 nm. Aminocoumarin is  
30 sold as CALCOFLUOR WHITE RWP Conc. or RW Solution. The  
aminocoumarins have an absorption maximum at 374.5 nm and  
an emission maximum at 450 nm.

Other examples of fluorescent colorants include rare  
earth metal chelates, and preferably, lanthanide  
35 chelates. Examples of lanthanide chelates include those  
formed by the chelation of organic ligands such as  
acetylacetone, benzoylacetone, dibenzoylmethane, and  
salicylic acid with lanthanide ions such as neodymium,

europium, samarium, dysprosium, and terbium ions.

- 5 Examples of such complexes include europium acetylacetonate, samarium acetylacetonate, neodymium benzoylacetonate, terbium salicylate, and dysprosium benzoylacetonate. The aforesaid chelates can be prepared by any suitable method known to those of ordinary skill
- 10 in the art. For example, a ligand such as acetylacetone can be reacted under suitable conditions with a rare earth metal halide such as europium trichloride to produce the rare earth metal chelate. For additional details, see U.S. Patent 4,736,425. The above chelates
- 15 absorb ultraviolet radiation and fluoresce in the visible range. The acetylacetonate of europium fluoresces with an emission line in the red region and this is particularly suitable for printing on white or light colored substrates. Examples of commercially
- 20 available rare earth chelate fluorescent colorants suitable for use in the ink composition of the present invention include, but are not limited to, the rare earth metal chelates sold as LUMILUX C<sup>TM</sup> pigments by Hoechst-Celanese Corp. in Reidel-de Haen, Germany.
- 25 The LUMILUX C rare earth metal organic chelates have a melting point of from about 130 °C to about 160 °C and a bulk density of from about 500 kg/m<sup>3</sup> to about 1100 kg/m<sup>3</sup>. Examples of organic LUMILUX C pigments include Red CD 316, Red CD 331, Red CD 332, Red CD 335, and Red CD
- 30 339, which are yellowish when unexcited and fluoresce in the orange-red region when excited by ultraviolet radiation. These pigments are soluble in organic solvents. Red CD 331, a preferred pigment and a derivative of europium-acetonate, is a yellowish powder
- 35 having an emission peak at 612 nm, a melting point in the range of 153-155 °C, and a density of 600 kg/m<sup>3</sup>. Red CD 331 is soluble in acetone, ethylacetate, ethanol, xylene, dichloromethane, dimethylformamide, n-hexane, and

dibutylphthalate. Red 316 is a rare earth  
5 acetylacetonate. Red CD 332, a rare earth biketonate,  
has a melting of 135-138 °C and a density of 500 kg/m<sup>3</sup>.  
Red CD 335, an europium chelate, has a melting point of  
133 °C and a density of 1030 kg/m<sup>3</sup>.

Additional examples of suitable LUMILUX pigments  
10 include Red CD 105, Red CD 106, Red CD 120, and Red CD  
131. These are inorganic pigments. Red CD 105 is white  
when unexcited, fluoresces in the orange-red region when  
excited by ultraviolet radiation, and has a median  
particle size of 7 microns. Red CD 106 is white when  
15 unexcited, fluoresces in the orange-red region when  
excited by ultraviolet radiation, and has a median  
particle size of 6 microns. Red CD 120 is white when  
unexcited, fluoresces in the red region when excited by  
ultraviolet radiation, and has a median particle size of  
20 2.7 microns. Red CD 131 is white when unexcited,  
fluoresces in the red region when excited by ultraviolet  
radiation, and has a median particle size of 6.5 microns.  
It is preferred that the particle size of the aforesaid  
pigments is further reduced by suitable means including  
25 grinding and crushing for use in the preparation of the  
jet ink composition.

Examples of other fluorescent colorants include the  
porphyrin type dyes described in U.S. Patent 5,256,193.  
These include, e.g., the tetra- chloride, bromide,  
30 tosylate, triflate, perchlorate, acetate, and  
fluoroborate salts of 5,10,15,20-tetrakis-(1-methyl-4-  
pyridyl)-21H,23H-porphine, 5,10,15,20-tetrakis-(1-  
hydroxymethyl-4-pyridyl)-21H,23H-porphine, 5,10,15,20-  
tetrakis-[1-(2-hydroxyethyl)-4-pyridyl]-21H,23H-porphine,  
35 5,10,15,20-tetrakis-[1-(3-hydroxypropyl)-4-pyridyl]-  
21H,23H-porphine, 5,10,15,20-tetrakis-[1-(2-  
hydroxyethoxyethyl)-4-pyridyl]-21H,23H-porphine, and  
5,10,15,20-tetrakis-[4-(trimethylammonio)phenyl]-21H,23H-

porphine. These colorants are excitable in the 380-500  
5 nm range, and fluoresce in the 600-800 nm range.

Any suitable amount of the colorant can be used to  
prepare the jet ink composition of the present invention.  
If the ultraviolet absorptivity or the fluorescent  
emission intensity is high, then a small amount of the  
10 colorant is sufficient. If the ultraviolet absorptivity  
or the fluorescent emission intensity is low, then the  
amount of the colorant used should be increased. The  
colorant is used preferably in an amount of from about  
0.01% by weight to about 1% by weight of the jet ink  
15 composition, and more preferably in an amount of from  
about 0.1% by weight to about 0.5% by weight of the jet  
ink composition.

#### INK CARRIER

20 The jet ink composition of the present invention  
comprises one or more solvents as the ink carrier. Any  
suitable solvent can be used in the preparation of the  
inventive jet ink composition, and preferably one or more  
organic solvents are employed. It is further preferred  
25 that the solvent evaporates rapidly under the printing  
conditions and without leaving behind a solvent residue.  
Organic solvents suitable for the preparation of the jet  
ink composition of the instant invention include ketones  
such as acetone, methyl ethyl ketone, diethyl ketone,  
30 cyclohexanone, and the like, esters such ethyl acetate,  
propyl acetate, butyl acetate, amylacetate, and the like,  
alcohols such methanol, ethanol, n-propanol, isopropanol,  
n-butanol, i-butanol, t-butanol, n-pentanol, n-hexanol,  
and the like. If desired, a mixture of solvents may be  
35 used.

Any suitable amount of the ink carrier can be used  
in the preparation of the jet ink composition of the  
present invention. The ink carrier is typically present

in an amount of from about 30% to about 80% by weight,  
5 and preferably in an amount of from about 60% to about  
75% by weight of the jet ink composition.

#### BINDER RESINS

The jet ink composition of the present invention  
10 comprises at least one binder resin which forms a film on  
the colorant. The binder resin also serves to improve the  
adhesion of the colorant and other ingredients to the  
printed surface. The binder resin is preferably  
colorless and thus does not impart visibility to the  
15 marks. Any suitable binder resin can be employed, and  
preferably a good film former is employed. A good film  
former rapidly forms a tough durable film as the result  
of the evaporation of the solvent.

It is preferred that the binder resin, or the main  
20 binder resin when a mixture of binder resins is employed,  
has a melting point or softening point above about 100  
°C. It is further preferred that the melting or  
softening point is about 120 °C or higher, and it is even  
further preferred that the melting or softening point is  
25 in the range of from about 120 °C to about 200 °C. In  
certain embodiments of the present invention, the melting  
point or softening point of the binder resin can be about  
150 °C or higher, especially for producing a mark that  
can survive the autoclaving treatment.

30 It is further preferred that the binder resin has  
low water absorption, preferably below about 3% by weight  
of the binder resin, and more preferably below about 1%  
by weight of the binder resin. It is also preferred that  
the binder resin has a low acid number, preferably below  
35 about 50, and more preferably below about 10. It is  
further preferred that the binder resin is soluble in  
common organic solvents such as ketones, alcohols, or  
esters.

Examples of suitable binder resins include

5 cellulosic resins such as nitrocellulose, cellulose acetate, cellulose acetate butyrate, and cellulose acetate propionate. Several grades of nitrocellulose, a preferred binder resin, are available commercially, e.g., from Hercules, Inc. in Wilmington, DE. These grades vary

10 in nitrogen content and viscosity. The nitrogen content of the nitrocellulose resin is preferably in an amount of from about 11% by weight to about 13% by weight, and more preferably in an amount of from about 11.8% by weight to about 12.2% by weight of the resin. Hercules' RS<sup>TM</sup> type

15 nitrocellulose has an average nitrogen content of 12% by weight and is available in a large number of viscosity grades, from 10 centipoises to about 2,000 seconds, measured on a 12.2% by weight solution in toluene. The nitrocellulose resin having low viscosities, e.g., a

20 viscosity of about 10-15 cps, is particularly preferred.

The RS type nitrocellulose resins have a softening point range of 155-220 °C, and the moisture absorption of unplasticized clear film at 21 °C in 24 hours in 80% relative humidity is 1% by weight.

25 Cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) can be obtained from Eastman Chemical, Kingsport, Tennessee. CAB-553-0.4 has a glass transition temperature of 136 °C and a melting point of 150 °C, and CAP-504-0.2 has a glass transition

30 temperature of 159 °C and a melting point of 190 °C.

The binder resin can be present in the jet ink composition in any suitable amount. It is preferably present in an amount of from about 5% by weight to about 15% by weight of the jet ink composition, and more

35 preferably in an amount of from about 10% by weight of the jet ink composition.

Certain embodiments of the jet ink composition include, in addition to the cellulosic resin, a silicone

resin. For example, it has been found that uncoated  
5 aluminum substrates can be printed advantageously using  
jet ink compositions containing nitrocellulose and  
silicone resins.

Any suitable silicone resin can be used, linear,  
branched or crosslinked, preferably those having a weight  
10 average molecular weight of from about 1000 to about  
10,000, more preferably those having a weight average  
molecular weight of from about 2000 to about 8000, and  
even more preferably those having a weight average  
molecular weight of from about 2000 to about 4000. A  
15 particularly preferred silicone resin is the DOW CORNING™  
6-2230 resin. The DC-6-2330 resin has a silanol content  
of 5% by weight of the resin, a weight average molecular  
weight of 2000-4000, and a degree of crosslinking of 1.2  
on a scale where 1.0 is completely crosslinked and 2.0 is  
20 fully linear.

The silicone resin can be present in the jet ink  
composition in any suitable amount. It is typically  
present in an amount of up to about 5% by weight of the  
jet ink composition, preferably in an amount of from  
25 about 1% by weight to about 3% by weight of the jet ink  
composition.

#### SURFACTANT

The jet ink composition may further contain a  
30 surfactant, which may be anionic, cationic, nonionic, or  
amphoteric. Examples of anionic surfactants include  
alkylbenzene sulfonates such as dodecylbenzene sulfonate,  
alkylnaphthyl sulfonates such as butyl or nonyl naphthyl  
sulfonate, dialkyl sulfosuccinates such as diamyl  
35 sulfosuccinate, alcohol sulfates such as sodium lauryl  
sulfate, and perfluorinated carboxylic acids such as  
perfluorodecanoic acid and perfluorododecanoic acid.  
Nonionic surfactants include the alkylesters of



polyethylene glycol, fatty acid esters of glycerol, fatty  
5 acid esters of glycol, and the like, and fluorochemical  
surfactants such as FC 170C, FC 430, FC 431, FC 740, FC  
120, FC 248, FC 352, FC 396, FC 807, and FC 824, which  
are available from 3M Co. FC 430 and FC 431 are  
fluoroaliphatic polymeric esters. Cationic surfactants  
10 include alkylamines, amine oxides, amine ethoxylates,  
alkyl hydroxyalkyl imidazolines, quaternary ammonium  
salts, and amphoteric surfactants include the  
alkylbetaines, the amidopropylbetaines, and the like.  
The surfactant may be present in the jet ink composition  
15 in any suitable amount. When a surfactant is used, it is  
typically used in an amount of from about 0.01% to about  
1% by weight of the jet ink composition, and preferably  
in an amount of about 0.1% by weight of the jet ink  
composition.,

20

#### PLASTICIZER

The jet ink composition of the present invention  
includes one or more plasticizers. It is believed that  
the plasticizer may also contribute to the improved  
25 properties of the marks, particularly the blush  
resistance. It is also believed that the hydrophobic  
plasticizer prevents or retards the diffusion of water,  
especially hot water, into the film formed by the binder  
resin.

30 Any suitable hydrophobic plasticizer can be used.  
Examples of suitable plasticizers include trialkyl  
phosphates, wherein the alkyl group can be branched or  
linear and have about 1 to about 10 carbon atoms,  
preferably about 3 to about 5 carbon atoms. A particular  
35 example of a suitable plasticizer is tributyl phosphate,  
which also acts as a flame retardant.

The plasticizer can be present in the jet ink  
composition in any suitable amount. It is typically

present in an amount of up to about 5% by weight, and  
5 preferably in an amount of from about 1% to about 3% by  
weight of the jet ink composition.

#### HIGH BOILING SOLVENT

The jet ink composition of the present invention may  
10 further contain a high boiling solvent, preferably a  
hydrophilic high boiling solvent. When the jet printed  
ink dries on the substrate, due to the evaporation of the  
volatile solvents, the mark can cool rapidly and absorb  
moisture from the surrounding. The absorbed moisture can  
15 impart a cloudy appearance to the film formed on the  
colorant. It has been observed that by including a high  
boiling hydrophilic solvent in the ink composition, it is  
possible to reduce or eliminate the development of  
cloudiness. The hydrophilic solvents have boiling points  
20 preferably above 100 °C, and more preferably in the range  
of from about 150 °C to about 250 °C.

Any suitable hydrophilic high boiling solvent known  
to those of ordinary skill in the art can be used.  
Examples of suitable high boiling solvents include  
25 glycols such as ethylene glycol, propylene glycol,  
glycerin, diglycerin, diethylene glycol, and the like,  
glycol ethers such as ethylene glycol dimethyl ether,  
ethylene glycol diethylether, cellosolve, diethylene  
glycol monoethylether (Carbitol), diethylene glycol  
30 dimethylether, and diethylene glycol diethylether dialkyl  
sulfoxides such as dimethyl sulfoxide, and other solvents  
such as sulfolane, N-methyl pyrrolidinone (NMP), and the  
like. NMP is a preferred high boiling solvent.

Any suitable amount of the high boiling solvent can  
35 be used, preferably in an amount of up to about 5% by  
weight of the jet ink composition, and more preferably in  
an amount of from about 2% by weight to about 4% by  
weight of the jet ink composition.

CONDUCTIVITY AGENT

5       The jet ink composition of the present invention  
further contains a conductivity agent which offers the  
desired electrical conductivity to the jet ink  
composition. It has been found that hygroscopic  
electrolytes tend to absorb water into the mark when  
10 exposed to high humidity or water. It is believed that  
the absorbed water forms micro-droplets in the film on  
the substrate. When water is later evaporated during  
drying of the marks, micro-voids are formed in the film,  
and the micro-voids scatter light. The difference  
15 between the refractive indices of the resin(s), which are  
generally greater than 1, and of air, which is 1, is  
responsible for the scattering effect. The scattering of  
light contributes to blushing.

It has been discovered that non-hygroscopic  
20 conductivity agents are effective in reducing or  
eliminating blushing. Any suitable non-hygroscopic  
conductivity agent can be used, preferably an organic  
salt is used. Examples of suitable organic salts include  
tetraalkyl ammonium salts and tetraalkyl phosphonium  
25 salts. The alkyl groups can be of any suitable number of  
carbon atoms, preferably about 1-10 carbon atoms, and  
more preferably about 2 to about 5 carbon atoms.  
Particular examples of preferred conductivity agents  
include tetraethyl or tetrabutyl ammonium or phosphonium  
30 salts. The salts can contain any suitable anion.  
Examples of suitable anions include chloride, bromide,  
and p-toluenesulfonate. Thus, particular examples of  
non-hygroscopic conductivity agents include tetraethyl  
ammonium chloride, tetraethyl ammonium bromide,  
35 tetrabutyl ammonium chloride, tetrabutyl ammonium  
bromide, tetrabutyl phosphonium chloride, tetrabutyl  
phosphonium bromide, and tetraethyl ammonium p-  
toluenesulfonate, which can be obtained from Aldrich

Chemical Co. in Milwaukee, WI.

5 Any suitable amount of the conductivity agent can be used to achieve the desired electrical conductivity. The agent is preferably present in the jet ink composition in an amount of from about 0.1% to about 2% by weight of the jet ink composition, and more preferably in an amount of  
10 from about 0.4% by weight to about 1.2% by weight of the jet ink composition.

The jet ink composition of the present invention can be prepared by any suitable method known to those of ordinary skill in the art. For example, the components  
15 can be sequentially added to a mixer and blended until a smooth ink composition is obtained. The ink composition can be filtered, e.g., using a 5-micron sock filter, to remove any impurities.

The following examples further illustrate the  
20 present invention but, of course, should not be construed as in any way limiting its scope.

#### EXAMPLE 1

This Example illustrates a preferred combination of  
25 the various ingredients of the jet ink composition of the present invention. IPA below stands for isopropanol.

<u>Materials</u>	<u>Preferred Range, Wt.%</u>
30 Acetone (Solvent)	about 50.0-about 95.0
Methanol (Solvent)	up to about 30.0
1-Methyl 2-Pyrrolidone (Solvent)	up to about 5.0
Nitrocellulose RS (10-15 cps, wetted with 30% IPA) (Binder)	about 5.0-to
35 about 15.0	
Silicon DC6-2230 (Binder)	up to about 5.0
Tetrabutylphosphonium Bromide (Conductive salt)	about 0.4-to about 1.2
Tributyl phosphate (Plasticizer)	about 1.0-to about 5.0
40 FC-430 (10% in acetone)	
(Surfactant)	up to about 1.0
UVITEX OB (Brightener)	about 0.1-to about 0.5

## EXAMPLE 2

5 This Example illustrates an optimal combination of ingredients of the jet ink composition of the present invention illustrated in Example 1.

	<u>Materials</u>	<u>Wt. %</u>
10	Acetone	62.5
	Methanol	19.5
	1-methyl-a-pyrrolidone	3.0
	Nitrocellulose	10.0
	Silicone DC6-2230	2.0
15	Tetrabutylphosphonium bromide	0.6
	Tributylphosphate	2.0
	FC-430	0.1
	UVITEX OB	0.3
20		<u>100.0</u>

A jet ink composition was prepared using the ingredients listed above by combining and mixing them until a smooth ink composition was obtained.

25

## EXAMPLE 3

This Example illustrates another preferred combination of the various ingredients that can be used to prepare a jet ink composition of the present invention.

30

	<u>Materials</u>	<u>Preferred Range, Wt%</u>
	Methyl ethyl ketone (Solvent)	about 30.0-to about
35	80.0	
	Methanol (Solvent)	about 10.0-to about 50.0
	1-Methyl 2-Pyrrolidone (Solvent)	up to about 5.0
	Nitrocellulose RS (10-15 cps, wetted with 30% IPA)	
40	(Binder)	about 5.0-to about 15.0
	Silicon DC6-2230 (Binder)	up to about 5.0
	Tetrabutylphosphonium Bromide (Conductive salt)	about 0.5-to about 1.5
45	Tributyl phosphate (Plasticizer)	about 1.0-to about 5.0
	FC-430 (10% in acetone)	

20

5

(Surfactant)	up to about 1.0
UVITEX OB (Brightener)	about 0.1-to about 1.0

10

## EXAMPLE 4

This Example illustrates an optimal combination of ingredients of the jet ink composition of the present invention illustrated in Example 3.

15	<u>Materials</u>	<u>Wt. %</u>
	Methyl ethyl ketone	61.65
	Methanol	20.0
	1-Methyl-2-pyrrolidone	3.0
	Nitrocellulose	10.0
20	Silicone DC6-2230	2.0
	Tetrabutylphosphonium bromide	1.0
	Tributylphosphate	2.0
	FC-430	0.1
	UVITEX OB	0.25
25		<u>100.00</u>

A jet ink composition was prepared using the ingredients listed above by combining and mixing them until a smooth ink composition was obtained.

30

## EXAMPLE 5

This Example illustrates another preferred combination of the various ingredients of the jet ink composition of the present invention.

35	<u>Materials</u>	<u>Preferred Range, Wt.%</u>
	Acetone (Solvent)	about 50.0-to about 95.0
	Duplicating fluid #5,	
40	anhydrous (Solvent)	up to about 30.0
	1-Methyl 2-Pyrrolidone	
	(Solvent)	up to about 5.0
	Nitrocellulose RS (10-15 cps,	
	wetted with 30% IPA)	
45	(Binder)	about 5.0-to about 15.0
	Silicon DC6-2230 (Binder)	up to about 5.0
	Tetrabutylphosphonium Bromide	
	(Conductive salt)	about 0.4-to about 1.2
	Tributyl phosphate	
50	(Plasticizer)	about 1.0-to about 5.0

## 21

- 5 FC-430 (10% in acetone)  
 (Surfactant) up to about 1.0  
 UVITEX OB (Brightener) about 0.1-to about 0.5

10

## EXAMPLE 6

This Example illustrates an optimal combination of the ingredients of the jet ink composition of the present invention illustrated in Example 5.

	<u>Materials</u>	<u>Wt. %</u>
15	Acetone	71.65
	Duplicating fluid #5, anhydrous (Solvent)	10.0
20	1-Methyl 2-Pyrrolidone (Solvent)	3.0
	Nitrocellulose RS (10-15 cps, wetted with 30% IPA) (Binder)	10.0
	Silicone DC6-2230	2.0
	Tetrabutylphosphonium Bromide	1.0
25	(Conductive salt)	
	Tributyl phosphate (Plasticizer)	2.0
	FC-430 (10% in acetone)	0.1
	UVITEX OB	0.25
30		<u>100.00</u>

- A jet ink composition was prepared using the ingredients listed above by combining and mixing them  
 35 until a smooth ink composition was obtained. Duplicating fluid #5 is ethanol denatured with isopropanol and n-propyl acetate.

40

## EXAMPLE 7

- This Example illustrates the properties of the marks produced from the inventive ink compositions set forth in Examples 2, 4, and 6. Metal cans from three different suppliers were employed in this study. The cans from  
 45 supplier 1 were made of aluminum, steel, and tin. The cans from supplier 2 were made of aluminum, and the cans from supplier 3 were made of steel and tin. The cans were subjected to testing under a variety of conditions.

## 22

The results obtained are set forth below and confirm that  
 5 the marks have excellent fading, bleeding and blushing  
 resistance.

<u>Cans From Supplier 1</u>		<u>Fading/Bleeding/Blushing*</u>		
		<u>Example 2</u>	<u>Example 4</u>	<u>Example 6</u>
10	Retort 250°F/30min (Cans filled w/98°C water)	No/No/0	No/No/0	No/No/0
	50°C/5min (Cans filled w/98°C water)	No/No/0	No/No/0	No/No/0
	40°C/5min (cans filled w/98°C water)	No/No/0	No/No/0	No/No/0
15	35°C/5min (cans filled w/98°C water)	No/No/0	No/No/0	No/No/0

Coated Cans From Supplier 2

20	Retort (125°C/30mins)	No/No/0	No/No/0	No/No/0
	Dipped in 100°C water/30min No/No/0	No/No/0		No/No/0
	Dipped in 80°C water/30min	No/No/0	No/No/0	No/No/0
	Dipped in 60°C water/30min	No/No/0	No/No/0	No/No/0
25	Dipped in 40°C water/30min	No/No/0	No/No/0	No/No/0

Uncoated Cans From Supplier 2

30	Retort (125°C/30mins)	No/No/1	No/No/1	No/No/1
	Dipped in 100°C water/30min No/No/0	No/No/0		No/No/0
	Dipped in 80°C water/30min	No/No/0	No/No/0	No/No/0
	Dipped in 60°C water/30min	No/No/0	No/No/0	No/No/0
35	Dipped in 40°C water/30min	No/No/0	No/No/0	No/No/0

Cans from Supplier 3

40	with red coating (150°F/5min)	No/No/0	No/No/0	No/No/0
	with black coating (150°F/5min)	No/No/0	No/No/0	No/No/0

\*Blushing is reported on a scale of 0-4. A blushing value  
 45 of 0 indicates absence of blushing, and a value of 1  
 indicates very slight blushing. A mark that exhibits  
 extreme blushing will be rated 4.



**CLAIMS:**

- 5           1.    A jet ink composition suitable for printing marks on metal, glass, plastics, rubber, or paper, the composition comprising an ink carrier, a fluorescent colorant, a cellulosic binder resin, and a tetraalkyl ammonium or phosphonium salt.
- 10           2.    A jet ink composition as claimed in Claim 1, wherein said composition has (1) a viscosity of from 1.6 to 7.0 centipoises at 25° C; (2) an electrical resistivity of from 50 to 2000 ohm-cm; and (3) a sonic  
15   velocity of from 1100 to 1700 meters/second.
3.    A jet ink composition as claimed in Claim 1 or 2, wherein said fluorescent colorant comprises 2,2'-(2,5-thiophenediyl)-bis(5-tert-butylbenzoxazole).
- 20           4.    A jet ink composition as claimed in any one of claim 1 to 3, wherein said cellulosic binder resin is nitrocellulose.
- 25           5.    A jet ink composition as claimed in claim 4, wherein said nitrocellulose has a nitrogen content of about 12% by weight.
6.    A jet ink composition as claimed in any one of  
30   the preceding claims, wherein said ink carrier comprises acetone, methyl ethyl ketone, methanol or ethanol.
7.    A jet ink composition as claimed in any one of the preceding claims, wherein said tetraalkyl ammonium or  
35   phosphonium salt is a tetrabutyl ammonium or phosphonium salt.

## 24

8. A jet ink composition as claimed in any one of  
5 the preceding claims further comprising a silicone resin.

9. A jet ink composition as claimed in any one of  
the preceding claims, further comprising a high boiling  
solvent such as N-methyl pyrrolidone.

10

10. A process of jet printing on metal, glass,  
plastic, rubber, or paper substrates, comprising  
projecting a stream of ink droplets of a jet ink  
composition as claimed in any one of the preceding claims  
15 to the surface of said substrates and controlling the  
direction of the stream electronically so that the  
droplets are caused to form the desired printed mark on  
the surface, said marks having blush resistance, bleed  
resistance, or fade resistance.

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/03404

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C09D B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 96 04335 A (SUBBARAMAN) 15 February 1996 see page 9, paragraph 1 see page 10, paragraph 1-2 see page 13, line 18-20 see page 17 - page 18 ---	1,4-10
Y	WO 90 01053 A (SIEMENS) 8 February 1990 see claims ---	1,4-10
A	FR 2 369 327 A (M & T CHEMICALS INC.) 26 May 1978 see claims ---	1,2,10
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

Internat J Application No  
PCT/GB 97/03404

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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